Translation

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Polyethylene Molding Material

It is the object of the invention to develop a polyethylene molding material on the basis of high-molecular ethylene polymerisates having high density with balanced property image, in particular with significantly increased viscosity and improved stress cracking resistance, while maintaining similar flow property and excellent rigidity.

This is attained in that said polyethylene molding material contains specific parts of a defined ethylene polymerisate of high density (Component B) and of a defined linear ethylene polymerisate of low density (Component C), as well as, perhaps, customary plastic additives, (Component D).

Application field for these polyethylene molding materials is the manufacture of molded bodies such as, for example, panels, pipes or foils.

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Description

The invention concerns a polyethylene molding material on the basis of high-molecular ethylene polymerisates of high density for the manufacture of molded bodies, such as, for example, panels, pipes or foils.

It is known that by preparing mixtures of ethylene polymerisates of high density and linear ethylene polymerisates of low density, it is possible to obtain molding materials having improved technical application properties (for example EP 66973). These mixtures, however, also inevitably result in particular properties of the molding materials which are undesirable for the specific processing method or for the manufacture of selected molded bodies. Among these is, for example, is a very large rise in the melt-flow index, occasioned by the utilization of linear ethylene polymerisates of low density and thereby [in] the flow capacity, as well as a clearly marked drop in the E-modulus resulting in significant rigidity loss of the molding material.

On the other hand, ethylene-polymers with ultra-high molecular mass are known which are largely excluded from processing by traditional processing methods, based on their properties, such as, for example, a melt-flow index which cannot be measured by traditional methods. They must first be brought into a sufficiently processable state by addition, for example, of larger amounts of frequently low-molecular substances, which is likewise connected with a loss in desirable property niveau of specific characteristic values. The ethylene polymer with ultra-high molecular mol-mass employed for said purpose traditionally presents a mono-modal mol-mass distribution (for example DE-OS 32139948).

The invention is based on the object of developing a polyethylene molding material on the basis of high-molecular ethylene polymerisates having high density with a balanced property image, in

particular excellent rigidity, significantly increased viscosity and improved resistance toward tension cracking without significantly affecting the original flow behavior.

According to the invention, the polyethylene molding material on the basis of high-molecular ethylene polymerisates of high density contains:

A) 40 to 90 mass percent of a high density ethylene polymerisate, having a density at 23°C of 0.940 to 0.955 g/cm^3, a melt-flow index MFI at 190°C and 49N from 0.4 to 1.0 g/10 min and a melt-flow index ratio as quotient of the MFI, with a load of 212 N and the MFI with a load of 49 N, from 10 to 30.

B) 5 to 45 mass percent of a high-density ethylene polymerisate having a density at 23°C of 0.940 to 0.960 g/cm^3, a viscosity number J from 500 to 1000 ml/g and a broad, preferably bi-modal mol-mass distribution, with a bi-modality parameter B from 1.02 to 2.0 and a distribution maximum with respect to mol masses greater than 800 000,

C) 2 to 40 mass percent of a low-density linear ethylene polymerisate, having a density at 23°C from 0.910 to 0.930 g/cm^3 and a melt-flow index MFI at 190°C and 21.2 N from 0.5 to 10 g/10 min, as well as

D) 0 to 5 mass percent of customary plastic additives, including stabilizers and coloring substances.

According to the invention, the polyethylene molding material on the basis of high-molecular ethylene polymerisates of high density is prepared by mixing the named starter components and subsequent granulation of the mixture.

Preferably employed are 55 to 75 mass percent of Component A, 15 to 25 mass percent of Component B, 4 to 20 mass percent of Component C and 0,2 to 1,0 mass percent of Component D.

The developed polyethylene molding material on the basis of high-molecular ethylene polymerisates of high density distinguishes itself in that it presents, in particular, a significantly increased viscosity, combined with good flow behavior, and an improved resistance toward the development of tension cracks, combined with good rigidity.

The invention is explained in more detail below, making use of several selected exemplary embodiments.

Example 1 (Reference Example)

As Component A, a high-density ethylene polymerisate was homogenized and granulated - said ethylene polymerisate in the form of a powder having been prepared by means of polymerisation according to the gas phase method, with 0.3 mass percent of a stabilizer mixture consisting of 50 mass percent penta-erythrityltetrakis-[3-(3.5-di-tert.butyl-4-hydroxyphenyl)propionate] and 50 mass percent Tris(2.4-di-tert-butyl-phenyl)phosphite - mixed in an asymmetric moved mixer - and on a two-screw extruder, with a screw diameter of 25 mm and a ratio of screw length to screw diameter of 32, homogenized and granulated at a melt temperature of 232^{O}C. The granulate presented the characteristic values indicated in the table with respect to density (DIN 53479), melt-flow index MFI at a temperature of 190^{O}C and a load of 49 N (DIN 53735), as well as

melt-flow index ratio MFR as quotient of the MFI, with a load of 212 N and the MFI at a load of 49 N.

After manufacture of test bodies according to norm from the granulate, the characteristical technical application values were ascertained as summarized in Table 3, with respect to notched bar test toughness according to Izod (DIN 53453), Tension-E-modulus (DIN 53457) and ductility (DIN 53455). Determination of resistance to tension cracking was done according to a modified stress/time-to-rupture test, similar to DIN 53449 Part 2 - involving test bodies having the size of 110 mm x 10 mm x 10 mm which were prepared from pressed panels with the dimension of 300 mm x 300 mm x 10 mm. As testing medium served ethylene glycol, at a test temperature of 80°C and a load of 5 Kp. The characteristic value listed in Table 3 is the quotient

$$Q = \frac{t_p}{t_s}$$

of the observed molding time for the actual test specimen t_p in hours and the observed molding time of the standard t_s in hours. The test specimen of Example 1 always served as standard reference.

Other properties listed in Table 3 are melt point as peak maximum and the crystallinity degree of the test specimens, which were determined by DSC measurements.

<u>Example 2 (Reference Example)</u>

In this example, a mixture was prepared consisting of a high-density ethylene polymerisate (Component A) and another high-density ethylene polymerisate, whose properties are in accordance with the specifications established for Component B.

The polymerisate employed in Example 1 served as Component A.

A polymerisate in powder form, which was likewise prepared according to the gas-phase method was used as Component B. A summary of the molecular parameters of said polymerisate with bi-modal mol-mass distribution is listed in Table 4.

Determination of the viscosity number J according to DIN 53728 at a temperature of 135°C in the solvent Dekalin (concentration of test solution: 0.00022 g polymerisate/cm^3 Dekalin, solution temperature: 150°C). High-temperature exclusion chromatography, at a temperature of 135°C in 1.2,4-trichloro-benzene was used in order to determine the mol-mass distribution. Characterization of the extent of the bi-modality of the mol-mass distribution was done by determining the bi-modality parameter B with

$$B = \frac{h_1 max + h_2 max}{2h^{min}}$$

whereby

h_1^{max}	stands for	peak height at the first maximum of the distribution
h_2^{max}	stands for	peak height at the second maximum of the distribution
h^{min}	stands for	peak height at minimum of distribution

(J. Schellenberg, B., Hamann: "Plaste und Kautschuk" 40 (1993) 225)

Both components were homogenized and granulated in the mixing proportions specified in Table 1 according to the conditions stated in Example 1, at a melt temperature of 236°C, as well as in the presence of 0.3 mass percent of the stabilizer mixture named in Example 1.

The results of Testing the different properties are shown in Tables 2 and 3.

Example 3

In this example, a polyethylene molding material was prepared according to the invention, consisting of two different high-density ethylene polymerisates (Component A and B) as well as a low-density linear ethylene polymerisate (Component C). The high-density ethylene polymerisates employed already in Examples 1 and 2 served as Components A and B. A linear low-density ethylene polymerisate with the properties listed in Table 5 was used as Component C.

Preparation of the molding material was done according to conditions listed in Example 1, at a temperature of approximately 240°C and the mixing composition specified in Table 1. For stabilization of the molding mass, 0.3 mass percent of the stabilizer mixture listed in Example 1 was likewise added.

The results of the different properties obtained after testing are represented in Tables 2 and 3.

The results clearly indicate that the molding material prepared in this example distinguishes itself in comparison with Examples 1 and 2, - at equal density and good traction-E-modulus, [which is even clearly higher vis-a-vis Example 1] - as well as similar melt-flow index - [still greater improvement vis-avis example 2] by significantly increased notched bar impact strength, significantly improved tension crack resistance as well as greater yield strength .

Examples 4 and 5

In these examples, additional molding materials were prepared on the basis of the polymerisates named in Examples 1, 2 and 3. The composition of the prepared mixtures is evident from Table 1. Here as well, addition was made of 0.3 mass percent of the stabilizer mixture indicated in Example 1. Preparation of granulate was done according to specifications of Example 1, with processing undertaken at a melt temperature of approximately 240°C. Property testing was done according to specifications of the same example; results are summarized in Tables 2 and 3.

The obtained characteristic values indicate that the molding materials prepared in these examples distinguish themselves vis-a-vis the reference examples 1 and 2, with similar melt index [vis-a-vis Example 2 still somewhat higher] and good rigidity, by significantly increased notched bar impact strength and significantly improved tension crack resistance, as well as greater yield strength.

In addition, these molding materials have a lower melting point and a lower degree of cristallinity, which, given similar rigidity, makes for easier processing of the molding material.

Example 6 (Reference Example)

For purposes of comparison, a molding material was prepared in this example which consisted of a high-density ethylene polymerisate (Component A from Example 1) and a low-density linear ethylene polymerisate (Component C from Example 3) in accordance with the specifications of Example 1, at a melt temperature of approximately 230^{O}C. The composition of the polymer components is shown in Table 1 and the properties of the molding material are specified in Tables 2 and 3.

It is apparent from the results that the flow capacity of the molding material - vis-a-vis the Reference Examples 1 and 2 - greatly increases in unwelcome fashion. Moreover, it is evident that the tension crack resistance does not increase in the desired fashion, but remains relatively constant. This makes it clear that in case of proceeding in a different than the inventive method, it is not possible to obtain the desired property combinations.

Table 1

Composition of the Mixtures

Example #	Component A [Mass %]	Component B [Mass %]	Component C [Mass %]	Component D [Mass %]
1	99.7	-	-	0.3
2	79.76	19.94	-	0.3
3	74.78	19.94	4.98	0.3
4	69.79	19.94	9.97	0.3
5	59.82	19.94	19.94	0.3
6	90	-	10	-

Table 2

Densities, Melt Indices & Melt Index Ratios of the Test Specimens

Example #	Density @23°C[g/cm^3]	MFI(190°C,49N) [g/10min]	MFR of Test Specimens
1	0.949	0.73	21.8
2	0.951	0.14	42.9
3	0.949	0.25	33.2
4	0.946	0.21	31.0
5	0.943	0.25	28.0
6	0.944	1.30	24.5

Table 3

Properties of the Test Specimens

Example #	Notch Impact strength @ 23°C [kj/m²]	Traction E Modulus [N/mm²]	Yield Strength %	Tension Crack Resistance Q	Melt Point [K]	Crystallinity Degree [%]
1	10.2	958	9.16	1	403.0	64.0
2	14.4	1017	9.33	0.94	403.9	64.9
3	16.8	999	9.71	1.87	403.9	62.0
4	18.1	908	9.83	1.33	403.4	60.7
5	21.7	819	10.43	1.60	402.6	57.9
6	-	-	-	1.04	-	-

Table 4

Properties of Component B from Example 2

Property	Characteristic Value
Density at 23°C	0.950 g/cm³
Viscosity No. J	730 cm³/g
Mol-mass Distribution:	
average mol-mass fig. M_n	36 400
average mol-mass vol. M_w	839 000
Lack of Uniformity U	22.1
Bi-modality Parameter B	1.11
First Maximum	2.0×10^5
Second Maximum	1.3×10^6

Table 5

Properties of the low-density linear Ethylene Polymerisate

Density	Characteristic Value
Density at 23°C	0.916 g/cm^3
Melt Index at Temperature of 190°C and Load of 21.2 N	2.2 g/10 min
Degree of Branching (measured by means of FT-IR)	0.91 CH_3/100 CH_2

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Patent Claims

1. Polyethylene molding material on the basis of high-molecular ethylene polymerisates of high density, containing

   A) 40 to 90 mass percent of a high-density ethylene polymerisate, with a density at 23°C of 0.940 to 0.955 g/cm^3, a melt-flow index MFI at 190°C and 49N of 0.4 to 1.0 g/10 min and a melt-flow index ratio MFR as quotient of the MFI at a load of 212 N and the MFI at a load of 49 N of 10 to 30.

   B) 5 to 45 mass percent of a high-density ethylene polymerisate, with a density at 23°C of 0.940 to 0.960 g/cm^3, a viscosity number J of 500 to 1000 ml/g and a broad, preferably bi-modal mol-mass distribution with a bi-modality parameter B of 1.02 to 2.0, and a maximum of distribution with mol-masses greater than 800 000,

   C) 2 to 40 mass percent of a low-density linear ethylene polymerisate, with a density at 23°C of 0.910 to 0.930 g/cm^3 and a melt-flow index MFI at 190°C and 21.2 N of 0.5 to 10g/10 min, as well as

   D) 0 to 5 mass percent of traditional plastic material additives, including stabilizers and coloring substances.

2. Polyethylene molding material on the basis of high-molecular ethylene polymerisates of high density according to Claim 1, prepared by mixing the named starter components and subsequent granulation of the mixture.

3. Polyethylene molding material according to Claim 1, containing 55 to 75 mass percent of Component A, 15 to 25 mass percent of Component B, 4 to 20 mass percent of Component C, as well as 0.2 to 1.0 mass percent of Component D.